RSET ANALYTICAL SUBCOMMITTEE ISSUE PAPER

DEVELOPMENT OF SQGS FOR PETROLEUM HYDROCARBONS

July 23, 2004 - Teresa Michelsen, Avocet Consulting and Jennifer Sutter, Oregon DEQ

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Question/Issue: What analytes and associated SQGs should be used for bulk petroleum hydrocarbons and/or their constituents, such as PAHs?

Background: Most existing SQG sets include guidelines for individual PAHs. To date, screening levels for bulk petroleum hydrocarbons in sediment have not been developed due to the widely varying mix of compounds that make up this group and the sense that toxicity was adequately accounted for by considering typical constituents of petroleum products (e.g., PAHs). However, there are situations where bulk petroleum hydrocarbons are present in sediment at elevated levels, and individual listed constituents either are absent or are present at levels that would not indicate toxicity. There has been limited analysis of whether these sediments pose a toxicity threat and in many cases the analysis for petroleum products is not performed. For cleanup sites in Oregon and some sites in Washington with heavy petroleum contamination, the policy has been to require bioassays to assess toxicity of petroleum-contaminated sediment; however, a consistent concentration above which bioassays would be required has not been established. Dredging programs in Washington and along the Columbia River have relied on SQGs for individual PAHs and sums of PAHs.

Recent work developing SQGs for a variety of areas along the west coast has identified issues with the predictiveness of individual PAH criteria. Specifically, PAHs do not appear to be associated with substantial toxicity on an individual basis, and in some cases can be dropped entirely from a data set without affecting the reliability of the resulting SQGs (Ecology 2003, Bay et al. 2004, Germano Assts. 2003). When added together on a dry weight basis, it is possible to see a relationship between the PAHs as a group and toxicity within the data set. However, this relationship is still prone to substantial error and is not a strong one. Taken together, these studies suggest the following conclusions:

- PAHs exhibit behavior that does not support a toxicity model in which these chemicals act independently of one another; rather some form of sum appears to better model their potential for toxicity

- Dry weight sums of individual PAHs alone may not accurately reflect the manner in which petroleum hydrocarbons express their additive toxicity and may introduce error into SQG calculations

These conclusions are consistent with what is known about petroleum toxicity to invertebrates, as discussed below. Furthermore, they suggest that existing individual PAH-based guidelines may be underprotective, especially in situations where substantial bulk petroleum exists.

Historically, regulation of bulk petroleum has largely occurred through total petroleum hydrocarbon (TPH) measurements, which are difficult to relate directly to toxicity. More recent theories for assessing the toxicity of petroleum and its constituents to benthic organisms have focused on a narcosis-based approach. Narcosis is a form of toxicity resulting from the presence of foreign molecules in hydrophobic or lipid tissues, which depresses and disrupts various cellular functions (Abernathy et al., 1988; Franks and Lieb, 1978). It is a well-studied phenomenon, as it is the basis for anesthesiology in medicine. Because narcosis represents a general disruption of basic cellular functions, which are essentially the same in all living organisms (microorganisms, invertebrates, fish, mammals, humans), the narcosis endpoint is applicable to any freshwater or marine aquatic receptor. Researchers have found that narcotic effects occur at similar tissue concentrations in a wide variety of aquatic receptors (Abernathy et al., 1988; McCarty and Mackay, 1993; McCarty, 1991; EPA, 1988).

In aquatic receptors, narcosis is manifested in various ways, including immobility, loss of equilibrium in fish, and mortality (McCarty et al., 1992; Rogerson et al., 1983; Bobra et al., 1985; Mackay and Hughes, 1984). These different manifestations are not really different endpoints, but rather can be thought of as a continuum of increasing responses to cellular dysfunction and shutdown. These effects are clearly related to population-level impacts, as they affect the ability of the organism to perform day-to-day functions, such as foraging, predator avoidance, and reproduction, and may finally result in mortality. Moreover, onset of narcosis effects would be expected at similar exposure concentrations for any member of an exposed assemblage of organisms, regardless of its taxonomic or community status.

In addition, the narcotic effect is not dependent on the specific lipophilic chemical or chemicals present (Call et al., 1985). Various studies (Ferguson, 1939; McGowan, 1952; Hermens et al., 1984; Hermens et al., 1985a,b; Deneer et al., 1988) have demonstrated that the narcotic effect is instead related to the total number of foreign molecules present, and therefore effects in tissue can be predicted from the total molar concentration of contaminants in the tissue. Thus it is not necessary to know the identity or toxicity of each individual chemical, just the molar concentration of all the chemicals in tissue combined. This property makes the narcosis endpoint particularly well-suited to the evaluation of toxic effects of petroleum (and other) mixtures in the environment, as a single sediment or tissue concentration can be selected that will be protective of aquatic receptors for a wide variety of lipophilic organic chemicals, assuming these chemicals do not have other, more specific interactions with the receptor causing toxicity.

Two methods could be employed to make use of this model in regulating petroleum constituents in sediments or tissues. First, individual PAH concentrations could be added together, normalized to a molar concentration or to a reference K_{ow} rather than using a dry weight sum (as is currently employed in the dredging program). K_{ow}-normalization is the basis of EPA's approach to regulating PAHs in sediments, authored by DiToro et al. (2000). Ecology recently compared the reliability of molar concentration sums vs. dry weight sums vs. individual PAHs during the development of the freshwater sediment quality guidelines (Ecology 2003). This comparison indicated that dry weight sums

showed greater association with toxicity in the data set than did the use of individual PAHs, and molar concentration sums showed greater association with toxicity in the data set than did dry weight sums. However, the overall reliability of the three data sets was approximately the same, indicating that there are errors associated with all three approaches. Most likely this is due to the use of individual PAHs to represent the entirety of the bulk petroleum present, when in fact all of the petroleum present contributes to narcosis toxicity.

Alternatively, bulk petroleum in the environment could be measured in molecular weight fractions, which would then be added together on a molar concentration basis to obtain a total petroleum concentration in molar units (μmol/kg). This approach is similar to methods adopted under the MTCA in Washington (WAC 173-340-740) and Massachusetts (MADEP 2002) to regulate petroleum hydrocarbons in soils. There is not currently enough VPH/EPH or TPH data in SEDQUAL to test whether this approach has better reliability than those that rely on individual PAHs.

Discussion: The following options are available for regulating individual PAHs and/or bulk petroleum products in sediments and tissues:

- Individual PAHs
- Dry weight sums of PAHs
- Molar or K_{oc}-normalized sums of PAHs
- Dry weight bulk measurements (e.g., TPH)
- Molar sum bulk measurements (e.g., VPH, EPH)

The individual PAHs and dry weight sums/bulk measurements have the advantage of being familiar, consistent with past practices, and consistent with current analytical techniques in widespread use. However, both in practice and in theory, these approaches do not appear to accurately model petroleum toxicity. The molar or K_{oc} normalized approaches, particularly those addressing bulk petroleum fractions, have the advantage of being consistent with toxicological theory and reflect the emerging scientific consensus with respect to petroleum toxicity and regulation. However, they rely on analytical techniques and calculation methods that are not currently in widespread use (though the methods do exist at a commercial level). Data would need to be collected using these analytical methods before the reliability of this approach could be definitively determined, as these measurements have not typically been done in sediments in the past.

It is worth noting that narcosis theory applies not only to bulk petroleum hydrocarbons, but also to any lipophilic compound that does not have a specific mode of action. Toxicologically speaking, narcosis effects would manifest as the sum of all such compounds. Narcosis-based water quality guidelines have been derived for pulp mill effluents as well as petroleum products in the Netherlands, for example. However, determining the molar concentrations of such complex mixtures requires monitoring and analytical techniques that are not currently in use in the United States. Nevertheless, it may be reasonable to add certain chemicals that are already being measured and are expected to have narcotic effects, such as phthalates and dibenzofuran, to the sum.

Proposed Next Steps:

- Policy committee and broader RSET discussion of these issues in September 2004 with comments forwarded to the SQG and Analyte subcommittees

- Analyte subcommittee to evaluate "doability" of VPH/EPH approaches in the region with respect to laboratories and costs, types of information obtained and how well it matches the needs of the toxicity models available; one question of particular interest is whether the majority of sediment-related bulk petroleum would be found in the EPH fraction, thus reducing the cost of the analysis

- SQG subcommittee to look at policy implications of changing from PAH to any bulk approach with respect to use of older data and development of new guidelines (it may be possible to develop them based on narcosis information already in the literature, followed by field-verification over time)

- SQG subcommittee also to eventually decide whether bulk measurements should 1) not be used, 2) replace PAHs, 3) be added to PAHs as SQGs, and in what form (e.g., dry weight vs. molar sums).

Interim Recommendations:

- Continue to evaluate petroleum at marine sites based on existing PAH criteria, and at freshwater sites based on criteria as recommended by the SQG subcommittee (currently under review).

- Consider bulk petroleum as a "Chemical of Special Occurrence" (per Section 8.4.2 of DMEF) at sites where petroleum is potentially a major issue (for example, crude oil or fuel spills, waterfront tank or pipeline leaks). EPH/VPH is the recommended analytical method as it provides differentiation of aliphatic and aromatic carbon ranges. Traditional bulk TPH analysis may be used as a screening tool to help map the distribution of bulk petroleum, but provides little value in predicting sediment toxicity.

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